Waste Management 34 (2014) 1836–1846

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Physicochemical and thermal characterization of nonedible oilseed residual waste as sustainable solid biofuel

Pooja Doshi *, Gopal Srivastava, Gauri Pathak, Madhurima Dikshit

Biochemistry Division, Department of Chemistry, University of Pune, Pune 411007, MS, India

ARTICLE INFO

Article history:
Received 10 August 2013
Accepted 18 December 2013
Available online 23 January 2014

Keywords:
Calorific value
Compressive strength
Chemical composition
Slagging–fouling
Pelletization
Thermogravimetric analysis

ABSTRACT

The present study aims to investigate the potential of nonedible oilseed Jatropha (*Jatropha curcas*) and Karanja (*Pongamia pinnata*) defatted residual biomasses (whole seed, kernel, and hull), as solid biofuel. These biomasses showed good carbon contents (39.8–44.5%), whereas, fewer amounts were observed for sulfur (0.15–0.90%), chlorine (0.64–1.76%), nitrogen (0.9–7.2%) and ash contents (4.0–8.7%). Their volatile matter (60.23–81.6%) and calorific values (17.68–19.98 MJ/kg) were found to be comparable to coal. FT-IR and chemical analyses supported the presence of good amount of cellulose, hemicellulose and lower lignin. The pellets prepared without any additional binder, showed better compaction ratio, bulk density and compressive strength. XRF analysis carried out for determination of slagging–fouling indices, suggested their ash deposition tendencies in boilers, which can be overcome significantly with the optimization of the blower operations and control of ash depositions. Thus, overall various chemical, physical properties, thermal decomposition, surface morphological studies and their high biofuel reactivity indicated that residual biomasses of Jatropha and Karanja seeds have high potential to be utilized as a solid biofuel.

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1. Introduction

Energy is considered as prime agent in the generation of wealth and a significant factor in economic development. The energy resources have been split into three categories: fossil fuels, renewable resources and nuclear resources. There are many alternative for new and renewable energy sources which can be used instead of the fossil and conventional fuels (Demirbas, 2000). As, the conventional or fossil fuels are becoming exhausted and contributing to greenhouse gas (GHG) emissions, leading to many negative effects on the global environment (Anon, 2005; Prasad et al., 2007; Singh et al., 2010; Zhao et al., 2009), the dominance of fossil fuels is gradually diminishing in favor of renewable sources of energy, including agricultural biomass (Serio et al., 2003; Xiao et al., 2001).

Lignocellulosic biomass represents a source of renewable energy. This biomass can be converted into liquid, solid and gaseous fuels with the help of some physical, chemical and biological conversion processes (Campbell, 1983; Ravindranath and Hall, 1995). Biomass has attracted attention as renewable energy sources with the highest potential to contribute to energy needs worldwide because of the ease of production and availability advantages as well as environmental benefits. In many developing countries, fraction of the biomass energy consumed is ranged from 40% to 50%, since these countries have large agriculture and forest areas (Ko and Bin, 2004). In addition to their sustainable favorability, they are, in general, more evenly distributed over earth's surface than fossil fuels or uranium and may be exploited using less capital-intensive technologies (Naik et al., 2010). Hence, they increase the scope for diversification and decentralization of energy supplies and the achievement of energy self-sufficiency at a local, regional and national level (Sudo et al., 1989). The Indian approach to biofuels is based solely on non-food feed stocks to be raised on degraded or wastelands that are not suited to agriculture, thus avoiding a possible conflict of fuel vs. food security (Mathiyazhagan et al., 2011). In India, a few states have created Boards, Authorities and Departments for the promotion and use of biofuels. Some have announced 'Minimum Support Price' for non feed oilseeds such as Karanja, Jatropha, Jojoba, Kusum, and Mahua (Kumar, 2010; Srivastava and Prasad, 2004).

Recently, Jatropha (*Jatropha curcas*) and Karanja (*Pongamia pinnata*) plants are receiving a great deal of attention (Achten et al., 2008; Kumar and Sharma, 2008; Openshaw, 2000) and were selected as the most suitable for production of biodiesel in India. Jatropha seed oil has been recognized as a source for medium viscosity pure plant oil that is easily converted to biodiesel with good product properties (Agarwal, 2007), based on its ability to thrive in a variety of agro-climatic conditions, a low gestation period, and high seed yield relative to other plants with oil-bearing seeds (Planning Commission, Government of India, 2003). It is apparent

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* Corresponding author. Tel.: +91 9545588772; fax: +91 02025691728.
E-mail address: pdoshi@chem.unipune.ac.in (P. Doshi).

0956-053X/$ - see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.wasman.2013.12.018

that extraction of biocrude or oil from the Jatropha seeds will generate huge quantity of residual deoiled seed cake. Jatropha production is forecasted about 2500 kg seeds/hectare under Indian conditions, and considering 40–50% oil in it, the extraction will generate approximately 1000 kg seedcake per hectare crop. Similarly, Karanja belonging to the *Leguminaceae* family is prominent species having nonedible oilseed that can be grown easily in available wastelands. In India, 0.93 million hectares of wastelands is covered with Karanja plantations in eight states (Kumar, 2010). The yield of oilseeds per tree is reported between 8 and 24 kg. The typical oilseed has oil 30–33% (Padhi and Singh, 2011). The availability of Karanja oilseeds and defatted oilseed cake in India is estimated to be around 0.20 and 0.145 million metric tonnes per annum respectively, before introduction of 'Biodiesel Programme' in the country (Radhakrishna, 2003).

One of the major problems arising in coming years will be disposal of defatted cake left over after expelling oil from these oilseeds (Chandra et al., 2006). Since Jatropha and Karanja are nonedible crops and the seeds are toxic (Akintayo, 2004; Gubitz et al., 1999), theses cakes cannot be used as cattle feed, unlike in other parts of the world where the vegetable oil from rape seed and soy, are used for biodiesel and their cake is used for cattle feed. Therefore, their safe disposal or meaningful utilization is very important. This residual waste, may be used either as animal feed after detoxification (Vinay and Sindhu Kanya, 2008) as organic nitrogenous fertilizers (Sanderson et al., 1996) or for biogas production (Chandra et al., 2006). Apart from these uses there is utmost need for development of its alternative applications. Thermal applications such as pellets and biofuels, are much more profitable as they are easier to materialize, require less financial investments and have a smaller environmental impacts (Gronalt and Rauch, 2007). Characterization of biomass is imperative as the chemical composition of biomass affects the combustion processes differently (Sanderson et al., 1996). From the chemical point of view this residual biomass is composite material, constituted by a mixture of hemicellulose, cellulose, lignin, inorganic matter (ash) and extractives, with proportion and chemical structure affected by variety (Theander, 1985; McKendry, 2002). The characterization techniques developed for other fuel like coal can also be applied for the biomass fuel (Carpenter, 2008). This characterization includes proximate analysis (moisture content, ash content, volatile matter), ultimate analysis (C, H, N, O, S), calorific value measurement, ash analysis and organic matter analysis. Therefore, knowledge of the influences of properties of final ash materials can make it possible to avoid fuel combinations with unwanted properties, or even to design an ash material for a certain application (Fernández et al., 2006; Theis et al., 2006). Several studies have dealt with co-combustion of biomass and coal (Amand et al., 2001; Werther et al., 2000; Okasha et al., 2006), as this fuel is attractive due to relatively high combustion efficiency, moderate NOx emissions and "intrinsic" sorbent retention capability. Eutectics of low melting point are created by absorption and chemical interaction between silica (SiO_2) and potassium compounds, e.g. K_2O or KCl of the ash biomass (Miles et al., 1996; Baxter et al., 1998; Ghaly et al., 1994). Also, researchers have confirmed and mentioned the formation of low melting point compounds like silicates in the combustion and gasification of lignocellulosic biomass (Lin and Dam-Johansen, 1999; Nordin et al., 1996; Ergudenler and Ghaly, 1992).

Further, these biomass materials are often preferred in densified form (briquettes, pellets, or cubes) than baled forms, which involve a lot of handling, transportation and storage costs, whereas, densification improves the effective bulk density of the biomass. Thus, the basic objectives of the present study was to evaluate the potential of residual biomasses left over after oil extraction from Jatropha and Karanja oilseeds for the production of solid biofuel. Hence, the defatted whole seed, kernel and hull biomasses were evaluated for their physicochemical characteristics and thermal decomposition as well as pelletization properties.

2. Materials and methods

2.1. Sample preparation

The dried whole seeds of Jatropha and Karanja were obtained from 'Agharkar Research Institute', Pune, Maharashtra, India as well as 'Indian Biodiesel Corporation', Baramati, Pune, Maharashtra, India. The whole seeds of both the seed samples were separated manually to obtain kernel and hull. Then, whole seed, kernel and hull were ground separately, using a mechanical grinder followed by laboratory defatting with solvent hexane using Soxhlet apparatus. These defatted residual biomasses were dried in oven at 70–80 °C overnight for removal of residual solvent, grounded, sieved (<250 mm) and stored in a separate air tight plastic containers till further used for characterization and pellet preparation.

2.2. Chemical characterization of residual samples

2.2.1. Proximate analysis

It involved moisture, ash, volatile matter and fixed carbon contents determination. To determine the moisture content, samples were introduced into hot oven at 105 °C till constant weight was achieved (ASTM 871-82, 2006).

The ash contents were determined using laboratory muffle furnace (Fourtech, Mumbai, India) as per the reported procedure (ASTM-D 3174-04, 2009). Briefly, 1.0 g of each residual biomass sample was taken in crucible and placed in muffle furnace and maintained at 600 ± 10 °C for 4 h. After cooling, the crucibles were removed from the furnace and placed in the desiccators. The above process of heating and cooling was repeated until constant weight was obtained, which allows the removal of volatiles and unburnt carbon.

The volatile matter was determined by the procedure given in ASTM-D 3175-07 (2009). The residual biomass samples (1.0 g each) were taken in crucible and placed in muffle furnace maintained at 950 ± 10 °C for 7 min. Then the crucibles were removed from the furnace and placed in the desiccators. The loss of weight was expressed as the volatile matter in the samples. The percentage of fixed carbon was determined by difference from 100, taking into account the percentile amounts of moisture, volatile matter and ash.

2.2.2. Ultimate analysis

The equipment used in this analysis was an elemental analyser (Vario EL III, Germany) available at ARI, Pune, with an automatic injector and the option of analyzing the C, H, N and S elements, simultaneously. The amount of oxygen was obtained by subtracting the sum of the C, H, N and S contents and the ashes from 100.

2.2.3. Biofuel reactivity

The biofuel reactivity was obtained from the proximate and ultimate analysis by dividing the volatile matter (VM) and fixed carbon (FC) contents in the sample along with the information provided by the molar ratios H/C and O/C (Miranda et al., 2008, 2009; Shafizadeh and DeGroot, 1976).

2.2.4. Chemical analysis

This involved cellulose, hemicellulose and lignin content determination in the residual biomass samples. The neutral detergent fiber (NDF) and acid detergent fiber (ADF) were determined using reported methods (Goering and Von Soest, 1975; AOAC (Association of Official Analytical Chemists), 1975).

The percentage of cellulose and hemicellulose was calculated using the following relation:

$$\text{Cellulose } (\%\text{ db}) = \text{ADF } (\%\text{ db}) - \text{Lignin } (\%\text{ db})$$

$$\text{Hemicellulose } (\%\text{ db}) = \text{NDF } (\%\text{ db}) - \text{ADF } (\%\text{ db})$$

2.2.5. FT-IR spectroscopy

To investigate functional groups in the samples, fourier transform infrared spectrometry (FT-IR) was employed, using Shimadzu FT-IR-8400 instrument available at our department. IR spectra of the samples were measured by using IR grade KBr. Samples were well mixed with KBr in the ratio of 1:9 respectively. All IR spectra were measured at 4 cm^{-1} resolution using IR range of 350–4000 $cm^{-1}$and scanning speed 15 scan/min in transmission mode.

2.2.6. Thermogravimetric analysis

Thermogravimetric (TG) and differential thermogravimetric (DTA) of biomass samples were simultaneously carried out using SHIMADZU-DTG-60H Thermal analyser (Shimadzu, Japan). About 10 mg sample each for Jatropha residues and Karanja residues were taken for analyzing devolatilization characteristics from 20 °C to 900 °C temperature at the rate of 10 °C/min under flowing nitrogen atmosphere with a flow rate of 50 ml/min.

2.2.7. Scanning electron microscope (SEM)

The scanning electron microscope (SEM) [JEOL, JSM-6360A, Japan] was used to examine the morphology of both raw biomass and ash particles. The sample powder was sprinkled as a thin layer on an adhesive tape placed on the brass sample holder. Excess amount of the sample was removed by blowing with the air spray. The adhered sample was then coated with gold powder using the sputtering device and then transferred into the JEOL sample chamber for the analysis. The accelerating voltage was set at 20 kV, 1000 time magnification and scale of 10 µm was selected.

2.3. Physical properties of pellets

2.3.1. Pellet preparation

The laboratory scale pellets were produced from known amount of residual biomass samples using hydraulic press machine (KBr Press, Techno search Instrument, India) and die punch (KBr Die, Technosearch Instrument, India) by applying pressure of 750 lb/in.^{2}. The pellets prepared were dried at 70–80 °C overnight and stored in airtight plastic containers till further analyses.

2.3.2. Volume reduction and compaction ratio

Initially volume before pelletization was measured by using measuring cylinder, wherein 1.0 g of the sample was taken in to measuring cylinder and tapped so as to consolidate at the base of the cylinder and volume of powdered biomass before pelletization was recorded. The volume of pellet was calculated according to its shape, height and radius. For measurement of height and radius of pellets, Vernier calliper (Timeter, US) was used (Tchobanoglous et al., 1993; Yazdanpanah et al., 2010). The volume reduction and compaction ratios were calculated as follows:

$$\text{Volume reduction } (\%) = [(V_i - V_f)/(V_i)]$$

$$\text{Compaction ratio} = [V_i/V_f]$$

where V_i is the initial volume, before pelletization and V_f is the final volume, after pelletization.

2.3.3. Bulk density

The volume and weight of the pellets were measured in order to determine the bulk density. Weight measurements were performed with a laboratory weighing balance. The volume of the pelletized and unpelletized samples was determined by using method described above (ASTM-D 690, 1974; Carpenter, 1998). Bulk density was calculated as the ratio of mass over volume of the bulk materials.

2.3.4. Compressive testing

Pellets were compressed along their cylindrical axis using Universal Tensile Machine, available at Dutech India Laboratories, Pune, as per the reported procedure (ASTM D 690). It was assumed that the pellets would be weakest in axial compression during combustion.

2.3.5. Calorific value

The calorific value of dried pellets (1.0 g each) was determined according to Indian standard (IS 1448 P:6), using a bomb calorimeter available at Chemtech Laboratories, Pune.

2.4. Elemental composition analysis of residual biomass by XRF

For the analysis of inorganic elements (Cl and oxides including SiO_2, Al_2O_3, K_2O, CaO, TiO_2, Na_2O, MgO, P_2O_5, MnO, Fe_2O_3), X-ray fluorescence spectrometer (AMETEK SPECTRO XEPOS) was used, available at Geology Department, University of Pune, Pune. Identification of compounds was made using the X-Lab Pro software.

The expressions of slagging and fouling indices (Carpenter, 1998) indicating ash deposition tendencies were carried out as follows:

$$\text{Base-to-acid ratio}:\ B/A = \frac{\%\ [Fe_2O_3 + CaO + MgO + K_2O + Na_2O]}{\%\ [SiO_2 + TiO_2 + Al_2O_3]}$$

$$\text{Silica—alumina ratio}:\ S/A = \frac{\%\ [SiO_2]}{\%\ [Al_2O_3]}$$

$$\text{Iron—calcium ratio}:\ I/C = \frac{\%\ [Fe_2O_3]}{\%\ [CaO]}$$

$$\text{Total alkalis}:\ TA = \%Na_2O + \%\ K_2O$$

3. Results and discussion

3.1. Characterization of residual samples

The results for proximate, ultimate, and chemical characteristics of defatted residual whole seed, kernel, hull and mixture samples obtained were as shown in Table 1.

3.1.1. Proximate analysis

The results obtained for moisture, volatile matter, ash and fixed carbon contents of Jatropha and Karanja biomass residual samples were as shown in Table 1. The moisture content was higher in hull of both the seeds, whereas, volatile matter was higher in kernel sample of both the seeds. It was observed that all the samples analyzed were having higher volatile matter contents (60.2–81.6%) as compared to the reported bituminous coal (35%) and lignite (29%), however, it was correlating well with that of other biomasses like wheat straw (59%), barley straw (46%). The ash contents of biomasses correlated well with other reported biomass samples like barley straw (6%), Lignite (6%), bituminous coal (9%), and wheat straw (4%) (McKendry, 2002). Thus, these finding for present samples suggested their greater facility to ignite even at low

Table 1
Properties of oilseed residual biomasses.

Defatted sample	*Jatropha curcas*			*Pongamia pinnata*		
	Whole seed	Kernel	Hull	Whole seed	Kernel	Hull
Proximate analysis (%)						
Moisture	9.4 ± 0.18	8.7 ± 0.20	10.2 ± 0.19	7.0 ± 0.16	5.6 ± 0.16	9.1 ± 0.24
Volatile matter	61.3 ± 0.82	66.7 ± 0.65	60.2 ± 0.75	78.1 ± 0.24	81.6 ± 0.58	71.3 ± 0.94
Ash	7.1 ± 0.14	8.7 ± 0.18	4.8 ± 0.16	4.6 ± 0.13	4.0 ± 0.15	5.2 ± 0.21
Fixed Carbon	22.3 ± 0.29	16.0 ± 0.45	24.9 ± 0.91	10.3 ± 0.31	8.8 ± 0.35	15.0 ± 0.61
Ultimate analysis (%)						
Carbon	39.8 ± 0.21	40.4 ± 0.39	42.9 ± 0.23	43.8 ± 0.15	43.2 ± 0.24	44.5 ± 0.37
Hydrogen	6.2 ± 0.19	6.5 ± 0.21	5.4 ± 0.24	6.4 ± 0.12	6.9 ± 0.28	6.4 ± 0.14
Oxygen	42.5 ± 0.23	36.3 ± 0.27	45.9 ± 0.17	41.5 ± 0.21	39.2 ± 0.16	42.0 ± 0.19
Nitrogen	4.0 ± 0.21	7.2 ± 0.33	0.9 ± 0.34	3.9 ± 0.23	6.1 ± 0.37	1.5 ± 0.21
Sulfur	0.56 ± 0.02	0.90 ± 0.07	0.15 ± 0.04	0.24 ± 0.02	0.63 ± 0.12	0.33 ± 0.05
Chemical analysis (%)						
Cellulose	31.5 ± 1.71	32.9 ± 1.84	29.8 ± 1.28	26.8 ± 2.01	28.2 ± 0.83	24.6 ± 1.81
Hemicelluose	22.7 ± 0.82	24.9 ± 1.31	17.2 ± 1.48	21.4 ± 0.99	23.1 ± 0.79	16.4 ± 0.86
Lignin	4.8 ± 0.21	3.5 ± 0.14	8.3 ± 0.19	3.8 ± 0.23	4.4 ± 0.25	9.4 ± 0.18

Note: The values represented are mean ± SD of triplicate determinations.

temperatures (Demirbas, 2005), higher heat transfer rates and advantageous at the problematic melting of the ashes (Goering and Von Soest, 1975).

3.1.2. Ultimate analysis

Typically, 30–40 wt% of the dry matter in biomass is oxygen. The principal constituent of biomass is carbon, making up from 30 to 60 wt% of dry matter depending on ash content. Of the organic component, hydrogen is the third major constituent, comprising typically 5–6% dry matter. Nitrogen, sulfur, and chlorine can also be found in quantity usually less than 1% dry matter but occasionally well above this (Jenkins et al., 1998). It was observed that all the residual samples do not vary much in their contents of carbon (39.8–44.5%) as represented in Table 1. Carbon content of present samples were comparable to reported carbon percentage of Indian coal (44.5%), but very less as compared to Indonesian coal (75.47%) (Muthuraman et al., 2010). The hydrogen content of all the samples analyzed was in the range (5.4–6.9%), which was comparable to hydrogen content of Indonesian coal (5.37%), but higher compared to Indian coal (3.33%) as reported by Muthuraman et al., 2010. However, the oxygen contents were in the range (36.3–45.9%), which was higher as compared to the reported oxygen content for Indian coal (5.55%) and Indonesian coal (16.4%). The difference in oxygen content of samples may be one of the contributing factors for difference in their calorific values as discussed below.

The nitrogen content of kernel sample of both seeds was relatively higher, being 7.2% and 6.1% respectively for Jatropha and Karanja. This findings were supported by reported literature, wherein, about 10.4–10.3% and 12.16–12.48% nitrogen content was observed for defatted Jatropha kernel meal (Chikpah and Demuyakor, 2012 and Srinivasan et al., 2013). High nitrogen content of kernel sample was indicative of its high protein content, which may create problems like emission of NOx gases if fired alone, thus requiring an additional measures (Khan et al., 2009). However, all the samples have shown lower sulfur content in the range (0.15–0.9%), thus indicating its advantage, as high sulfur content may generate SO_2 gases during the combustion process leading to harmful effect on environment (Dayton et al., 1995). Sulfur and chlorine are also involved in certain ash reactions leading to fouling and slagging of ashes in boilers (Jenkins et al., 1998). The often-cyclical nature of biomass fuel can easily be addressed in a co-firing arrangement by appropriately adjusting the coal: biomass blend ratio. As biomass contains generally low concentrations of sulfur and nitrogen, co-firing can reduce SO_2 emissions and in most cases also NOx emissions from coal-fired power plants (Baxter, 2005; Van Loo and Koppejan, 2008).

3.1.3. Biofuel reactivity

The differences in biofuel reactivity determining factors i.e. ratios of H/C, O/C and VM/FC for all residual biomass samples obtained were as shown in Fig. 1. It was observed that VM/FC ratios were varying largely in the range 2.43–9.27% for whole seed, kernel and hull sample, being relatively higher for Karanja residual samples as compare to Jatropha residues. Interestingly, the analyzed residual biomasses were found to be highly reactive as compared to other reported biomasses viz. palm waste, corn waste, wheat straw usually used for energy production (Miranda et al., 2009). Thus, these results of present residual biomass samples suggested their advantage over other biomasses for utilization as solid biofuel.

3.1.4. Chemical analysis

Cellulose is a polymer of β-D glucopyranose units, hemicelluloses posses variable composition of five and six carbon and lignin is an irregular polymer of phenylpropane units (Chum and Baizer 1985; Schultz and Taylor, 1989; Wyman and Hinman, 1990; Lynd, 1990). The composition of cellulose, hemicellulose and lignin obtained were as represented in Table 1. The contents of cellulose and hemicelluloses were relatively higher in kernel sample of both

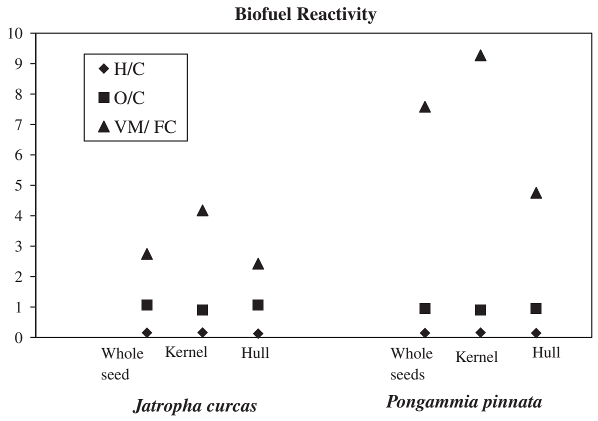


Fig. 1. Biofuel reactivity of *Jatropha curcas* and *Pongamia pinnata* oilseed residual biomasses.

the seeds as compared to whole seed and hull samples, whereas, lignin content was higher in hull of both the seed samples. These differences in chemical composition may contribute to the variation in calorific values of pelletelized samples as presented in Table 4. The components of biomass not only include cellulose, hemicelluloses, lignin, but also lipids, proteins, simple sugars, starches, water, hydrocarbons, ash and other compounds. Due to the carbohydrate structure, biomass is highly oxygenated with respect to conventional fossil fuels including hydrocarbons liquids and coals (Khan et al., 2009).

3.1.5. FT-IR spectroscopy

The FT-IR data obtained for all residual biomasses (Table 2), showed the presence of alkane, alkene and carbonyl functional groups in all the samples. The most prominent peaks in the spectrum originated from –OH stretching vibration 3370–3420 cm^{-1} and CH_2 and CH_3 asymmetric and symmetric stretching vibrations 2935–2915 cm^{-1} indicated the presence of hemicellulose, cellulose and lignin (Naik et al., 2010; Thipkhunthod et al., 2007). The remaining strong band at 1030 cm^{-1} contributing to C–O bonding were also supposed to be cellulose structure belonging. The lower absorption band at 2800–3000 cm^{-1} and 1400 cm^{-1} of extracted residue indicates the loss of aliphatic carbon and carboxylic group. The standard method suggests these extractives to be waxes, fats, resins or oils (Thipkhunthod et al., 2007). Peaks in the region 1742–1620 cm^{-1} were originated from the stretching mode of carbonyls mainly ketones and esters (Himmelsbach et al., 2002). Hence, in the present samples these peaks may be due to oil remained in the samples after defatting. Also, peaks in the spectrum originate from aliphatic C—H deformation 1300–1500 cm^{-1} and the remaining weak band at 1590–1700 cm^{-1} contributing aromatic carbon vibration indicated the unique lignin characteristic (Sharma et al., 2004). The presence of protein constituent was also confirmed by the presence of remaining N—H spectra at 3100–3600 cm^{-1}.

3.1.6. TGA and DTA analysis

Lignocellulosic structure of biomass can be qualitatively identified from thermogravimetry analysis. The weight losses observed in TG and DTA curves are reported to be relevant to the devolatilization of cellulose, hemicelluloses, and lignin fractions in biomass, which significantly influence the pyrolysis behavior (Aguiar et al., 2008; Biagini et al., 2006; Chen and Kuo, 2010; Hu et al., 2007; Zabaniotou et al., 2008). Non-isothermal thermogravimetric analysis (TGA) is proved to be one of the best methods for understanding the pyrolysis behavior and it has been extensively used at low heating rates and temperatures up to 900 °C (Saddawi et al., 2010). In general, the pyrolysis process can be divided into three stages: moisture evaporation, main devolatilization and continuous slight devolatilization (Ounas et al., 2011).

Biagini et al., 2006 used xylan as a standard molecule for hemicellulose, the onset temperature was 253 °C and maximum weight loss was at 299 °C. The volatile matter released after primary devolatization was 76.3 wt%. Similarly, in cellulose the onset temperature was 319 °C and maximum devolatization occurred at 354 °C. The volatiles released after the primary step of devolatization was 79.6 wt%. Whereas, in case of lignin it is decomposed in a wider range of temperature compared to hemicellulose and cellulose. The onset temperature was comparable to xylan. However, the primary devolatilization could be completed at 482 °C. The maximum weight loss was occurred at 361 °C. The final weight loss in case of lignin (60.2 wt%) was lowest in compared to hemicellulose and cellulose.

TGA curves for Jatropha; Fig. 2(a, b, c) and for Karanja; Fig. 3(a, b, c) respectively for whole seed, kernel, hull, represents mass loss (TGA) and derivative mass loss (DTA) curves at 10 °C/min under inert atmosphere. In TG–DTA curves of Jatropha, Fig. 2 the main thermal decomposition of lignocellulosic materials generally occurs over the temperature range of 200–400 °C. Lignin is the first component to decompose at a low temperature and low rate and continues on until approximately 900 °C. Hemicellulose is a light fraction component which decomposes between 160 and 360 °C. Cellulose is the last component to decompose in the temperature range of 240–390 °C (Aguiar et al., 2008; Vamvuka and Zografos, 2003). There were two major peaks observed in Jatropha TG–DTA curves, the first peak could be generated by the decomposition of hemicellulose and some of the lignin and the second peak should correspond to the decomposition of cellulose and the remaining lignin (Font et al., 2009; Raveendran et al., 1996). Whereas, in Fig. 3 for Karanja residual samples, the onset temperature of devolatilization was observed in the range of 57–140 °C. Weight loss in the range 140–250 °C could be attributed to decomposition of hemicellulose. The main weight loss approximately 50% in the range of 250–370 °C could be due to cellulose degradation followed by a slow and continuous weight loss as discussed above. The former step of weight loss may be due to the primary devolatilization, whereas, the later can be attributed to the degradation of heavier chemical structures in the solid matrix (Fisher et al., 2002).

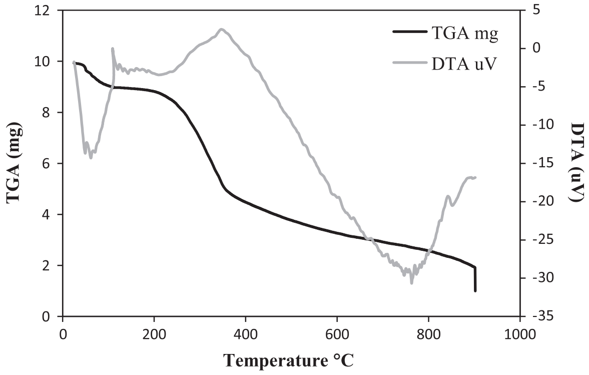
3.1.7. Scanning electron microscopy (SEM)

Morphological change of the simulated and actual biomass samples before and after combustion were observed by a scanning electron microscope, Fig. 4 (a) whole seed (b) kernel and (c) hull for *Jatropha curcas*, Fig. 5 (a) whole seed (b) kernel and (c) hull for *Pongamia pinnata*. Physical appearance of all the biomasses analyzed and their ashes were quite different. The SEM photographs indicated that these material posses, diverse morphology in terms of amorphous flakes, lumpy granular and polygonal lamellar porous structures. Ashes of the biomass after heating at 600 °C showed the microstructure including smooth, polygonal, granular and molten drop characteristics. A large percentage of structures present in ashes are commonly 1–20 μm in size and appears to contain agglomerates of the small sized particles. These observations are supported by similar observations reported by Bakisgan et al. (2009), for wheat straw, olive bagasse and hazelnut shell samples.

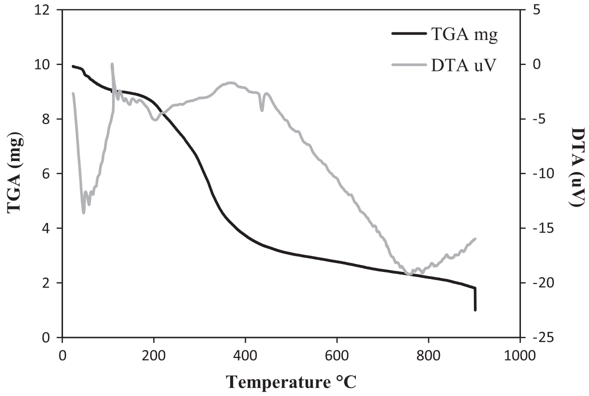
Table 2
Absorption peak detected and corresponding functional group of oilseed residual biomasses.

Wave number	Functional group
Broad band 3100–3600 cm^{-1}	O—H vibration of carboxylic and alcoholic groups H-bonded N—H groups
Peaks between 3370 and 3420 cm^{-1}	—OH stretching vibration
Peaks between 2800 and 3000 cm^{-1}	Aliphatic C—H stretching
Peaks between 2935 and 2915 cm^{-1}	CH_2 and CH_3 asymmetric and symmetric stretching vibrations
Peak at 1720 cm^{-1}	C═O stretching of COOH and ketonic and carbonyls
Band at 1640 cm^{-1}	C═C in aromatics structure
Band at 1300–1500 cm^{-1}	Aliphatic C—H deformation
Peak at 1400 cm^{-1}	C—H and OH of COOH
Peaks between 1000 and 1100 cm^{-1}	C—O stretching of carbohydrate and alcohol function and reflect the occurrence of polysaccharides or cellulose

(a) Whole seed



(b) Kernel



(c) Hull

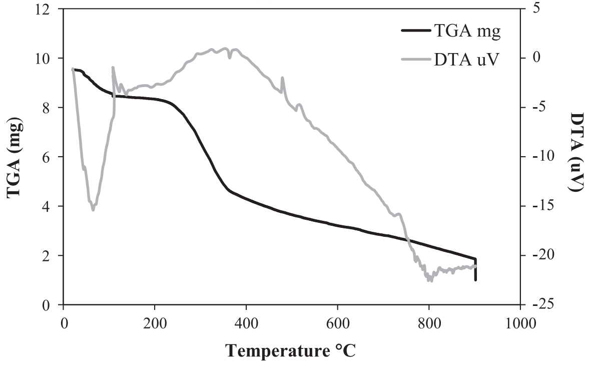
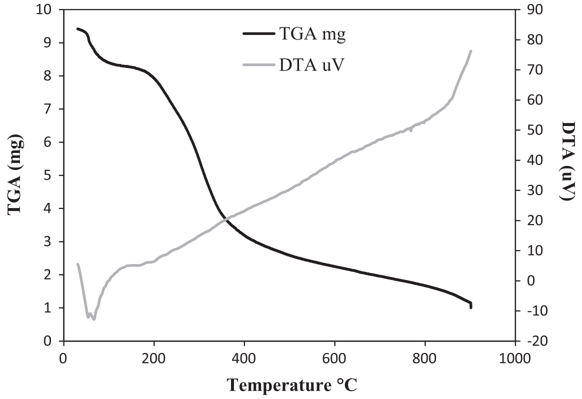


Fig. 2. TGA–DTA curve of *Jatropha curcas* oilseed residual biomasses: (a) whole seed, (b) kernel and (c) hull.

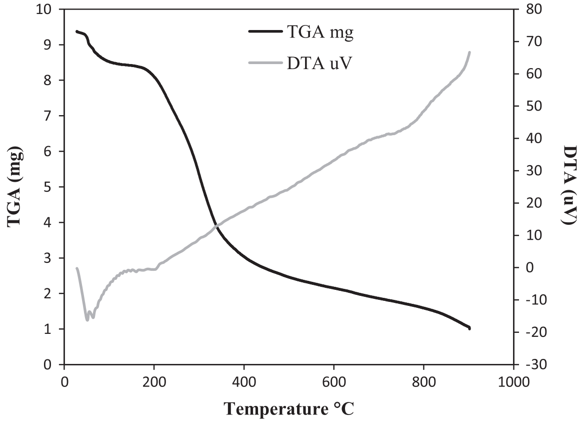
3.2. Pellet characteristics

Pellet prepared using hydraulic press was cylindrical in shape. In the pelletizing process, raw material is dried, ground, homogenized, and densified, which improves transport, storage, and handling characteristics (Larsson et al., 2008). The pelletized fuel due to higher density contains more energy per volume than unpelletized material (Sokhansanj and Turhollow, 2004). This source allows for regular void spacing, which assists in the passage of gasses through the combustion system (Saxena, 1988). Dust and odours are also minimized since the fuel pellets are homogenized and smaller particles get trapped into the material matrix. The pelletized material of good compressive strength is always selected as it can maintain its structural integrity for longer time during combustion (Marsh et al., 2007). Pellets are the solid biofuel that has the highest refining degree compare to firewood, bark, forest chip (stem chip, green chip), and chips from demolition waste, briquettes. In combustion plant of solid biofuel, degrees of refining represents it's compositional, operational and maintenance properties. Other advantages with highly refined biofuels are storage capacity and a simpler regulation of the combustion process. Lignin present in the samples may be acting as binder, thus, pellets prepared does not require any artificial binder (Chung, 1991).

(a) Whole seed



(b) Kernel



(c) Hull

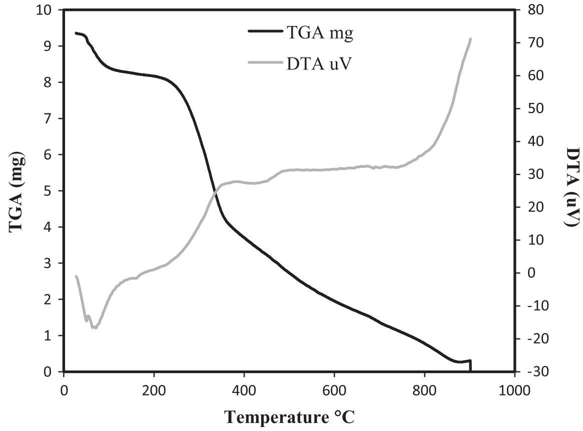
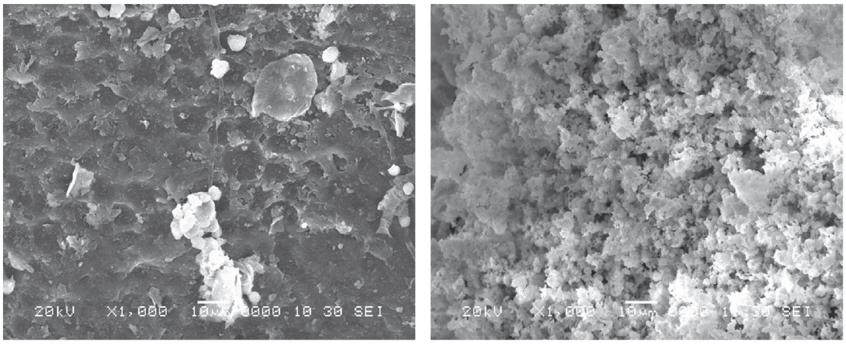


Fig. 3. TGA–DTA curve of *Pongamia pinnata* oilseed residual biomasses: (a) whole seed, (b) kernel and (c) hull.

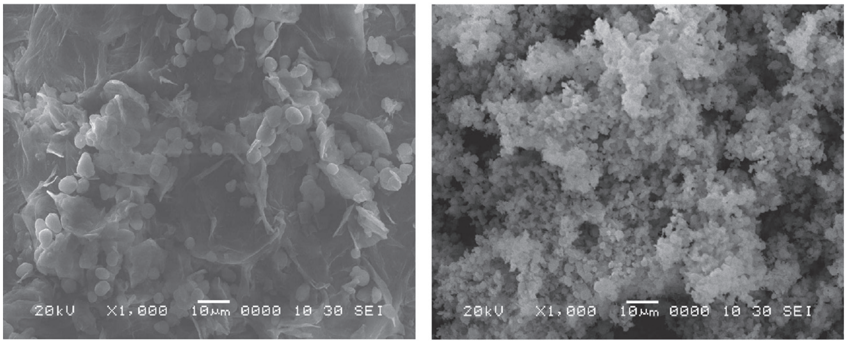
3.2.1. Volume reduction and compaction ratio

Volume reduction and compaction ratio obtained using information provided by volume of samples before and after pelletization were as represented in Table 3. Volume of powdered kernel sample was relatively higher as compared to hull and whole seed

(a) Whole seed


Before ashing After ashing
20kV X1,000 10µm 0000 10 30 SEI
20kV X1,000 10µm 0000 10 30 SEI

(b) Kernel


Before ashing After ashing
20kV X1,000 10µm 0000 10 30 SEI
20kV X1,000 10µm 0000 10 30 SEI

(c) Hull

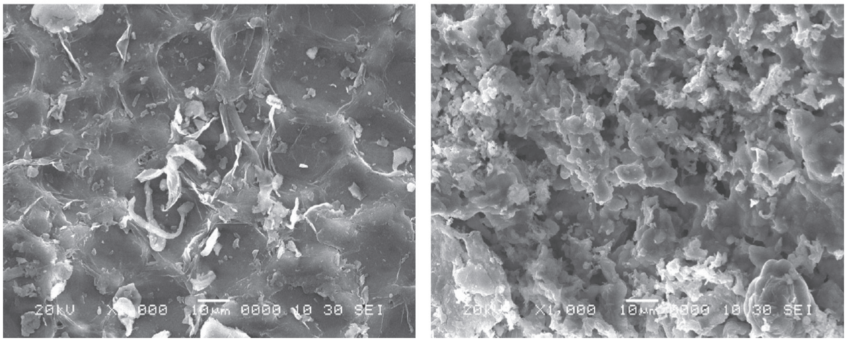

Before ashing After ashing
20kV X1,000 10µm 0000 10 30 SEI
20kV X1,000 10µm 0000 10 30 SEI

Fig. 4. Scanning electron microscope images of *Jatropha curcas* oilseed residues before and after ashing.

samples for both Jatropha and Karanja (1 g sample each), being 4.05 cm^3 and 1.36 cm^3 and its volume after pelletization was 0.88 $cm^3$and 0.26 cm^3 respectively. Whereas, volume of powdered hull samples was 1.38 cm^3 and 0.9 cm^3 and volume of hull pellets were 0.84 cm^3 and 0.3 cm^3 respectively for Jatropha and Karanja. These results indicated the presence of more void volume in case of powdered kernel samples, while less in powdered hull samples of both Jatropha and Karanja. The higher volume reduction in kernel sample correlated well to its high compaction ratio, whereas, low volume reduction in hull sample correlated to its low compaction ratio as represented in Table 3.

3.2.2. Bulk density

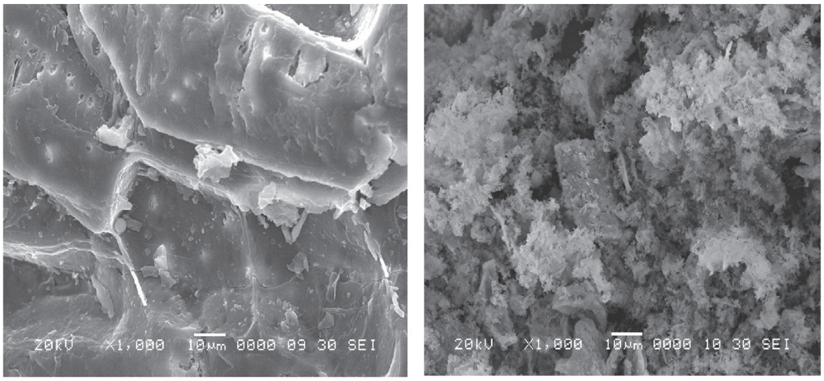
Values for bulk density of pelletelized and unpelletlized samples were obtained as given in Table 3. The bulk density of pelletelized samples (1.14–1.86 g/cm^3) was higher as compared to that of unpelletlized samples (0.25–0.72 g/cm^3). Direct relation was found between bulk density and volume reduction during pelletization. This explains higher bulk density of the pelletelized kernel sample than other samples, which correlates well with its higher volume reduction and compaction ratio.

It has been demonstrated that the density increases as the empty spaces between the particles decreases. Thus, after applying pressure during pelletization particles come closer, resulting in higher bulk density of pellets. It is reported that bulk density negatively correlates to moisture content in raw materials (Rhen et al., 2005) which, correlated well with lower bulk density of hull pellets having maximum moisture content. In biomasses, properties like bulk density were also correlated to the fuel preparation methods (Demirbas, 2004).

3.2.3. Compressive testing

From Table 4 it can be observed that all the sample pellets were having very good compressive strength and could withstand maximum up to 1065 kg. Thus, the pelletization of present samples without adding any external binder suggests positive characters

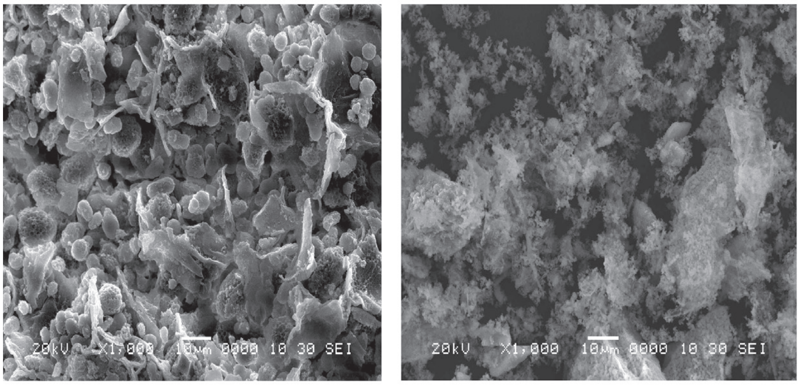
(a) Whole seed



Before ashing After ashing

20kV X1,000 10µm 0000 09 30 SEI
20kV X1,000 10µm 0000 10 30 SEI

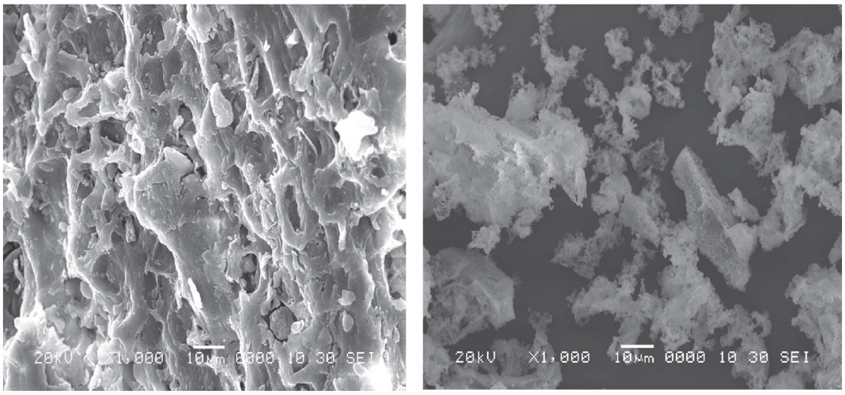
(b) Kernel



Before ashing After ashing

20kV X1,000 10µm 0000 10 30 SEI
20kV X1,000 10µm 0000 10 30 SEI

(c) Hull



Before ashing After ashing

20kV X1,000 10µm 0000 10 30 SEI
20kV X1,000 10µm 0000 10 30 SEI

Fig. 5. Scanning electron microscope images of *Pongamia pinnata* oilseed residues before and after ashing.

Table 3
Volume reduction (%) and compaction ratio of oilseed residual pellets.

Pelletization properties of defatted sample	Volume of biomass (V_i) (cm^3)	Volume of pellet (V_f) (cm^3)	Volume reduction (%)	Compaction ratio
Jatropha curcas				
Whole seed	2.6 ± 0.06	0.84 ± 0.01	0.68 ± 0.01	3.12 ± 0.09
Kernel	4.05 ± 0.06	0.88 ± 0.43	0.78 ± 0.01	4.64 ± 0.01
Hull	1.38 ± 0.03	0.84 ± 0.02	0.41 ± 0.01	1.64 ± 0.03
Pongamia pinnata				
Whole seed	1.16 ± 0.04	0.28 ± 0.05	0.75 ± 0.01	4.31 ± 0.22
Kernel	1.36 ± 0.04	0.26 ± 0.00	0.80 ± 0.01	5.06 ± 0.17
Hull	0.9 ± 0.00	0.30 ± 0.00	0.66 ± 0.00	2.98 ± 0.00

The values represented are mean ± SD of triplicate determinations.

Table 4
Bulk density, compressive strength and calorific value of oilseed residual pellets.

Pellet type	Bulk density of unpelletized biomass[a] (g/cm^3)	Bulk density of pellet[a] (g/cm^3)	Compressive strength[a] (kg)	Gross calorific value (MJ/kg)
Jatropha curcas				
Whole seed	0.38 ± 0.02	1.19 ± 0.01	348.3 ± 59.25	18.61
Kernel	0.25 ± 0.004	1.14 ± 0.02	181.1 ± 35.32	18.96
Hull	0.72 ± 0.02	1.20 ± 0.03	376.2 ± 5.373	17.68
Pongamia pinnata				
Whole seed	0.43 ± 0.017	1.77 ± 0.03	1065.1 ± 64.37	18.72
Kernel	0.37 ± 0.012	1.86 ± 0.01	935.0 ± 45.62	19.98
Hull	0.56 ± 0.00	1.66 ± 0.02	934.3 ± 25.71	18.91

[a] The values represented are mean ± SD of triplicate determinations.

Table 5
Elemental compositions of oilseed residual biomass ashes (%)[a].

Symbol	Element	*Jatropha curcas*			*Pongamia pinnata*		
		Whole seed (%)	Kernel (%)	Hull (%)	Whole seed (%)	Kernel (%)	Hull (%)
SiO_2	Silicon	<0.0011	<0.0011	2.565	6.181	12.92	<0.0011
Al_2O3	Aluminum	<0.0038	<0.0038	0.61	0.526	1.435	1.15
K_2O	Potassium	28.68	32.09	31	47.77	40.2	45.0
CaO	Calcium	18.1	13.29	25.22	31.2	34.37	26.42
TiO_2	Titanium	0.0158	0.0598	0.0747	0.2356	0.4245	0.0673
Na_2O	Sodium	<0.014	<0.014	3.89	<0.014	<0.014	<0.014
MgO	Magnesium	28.42	24.1	24.52	27.58	18.85	23.39
P_2O_5	Phosphorus	37.38	55.23	3.868	34.46	59.63	3.509
MnO	Manganese	0.1326	0.0872	0.1971	0.1599	0.1654	0.1552
Fe_2O_3	Iron	0.5828	0.4463	0.5552	1.26	2.246	0.4385
Cl	Chlorine	1.7640	1.0390	1.7550	0.6487	0.7620	1.7130

[a] The values represented are mean of duplicate determinations.

towards its use for energy production. High compressive strength avoids damage to pellets during transportation and also maintains its structural integrity inside boiler, gassifier, etc. during combustion**.** Also, void spacing can only be maintained if pellets hold their structure during the devolatisation process (Saxena, 1988; Marsh et al., 2007). It is therefore important that the pellets have a good compressive strength. Compressive testing was chosen to illustrate changes in the physical properties of the pellets because the pellets were formed using a compressive force in the Hydraulic pressure machine. Jatropha oilseed residue showed low compressive strength as compared to karanja, but it was similar to other biomasses like barley straw (481.81 kg), canola straw (465.90 kg), oat straw (471.61 kg) and wheat straw (477.94 kg) at 448.67 kg applied load (Adapa et al., 2009).

3.2.4. Calorific value

The calorific value which determines the quantitative energy content (Khan et al., 2009), of the pelletized samples varied as shown in Table 4. The Karanja kernel pellet was having higher calorific value (19.98 MJ/kg) than other samples in spite of similar carbon and hydrogen contents, which could be attributed to its less oxygen (Demirbas, 2004). Further, it was observed that calorific value of Karanja hull pellet (18.91 MJ/kg) was lower than that of kernel pellet, this may be due to higher ash content of hull sample than that of kernel sample (Table 1), which correlates well with the reported literature that, higher the ash content of the raw material, lower the calorific value (Bassam et al., 2004). Overall, the gross calorific values for all residual biomass samples were comparable with that of reported biomasses like cereal straw (17.30 MJ/kg), bagasse (19.40 MJ/kg), switchgrass (17.40 MJ/kg), poplar and miscanthus (18.50 MJ/kg) (McKendry,2002). This result also suggests the advantage of present sample for production of solid biofuel.

Table 6
Slagging and fouling indices of oilseed residual biomasses.

Sample	B/A ratio	S/A ratio	I/C ratio	Total alkalies (TA)
Jatropha curcas				
Whole seed	3660.23	0.30	0.032	28.69
Kernel	1086.03	0.30	0.034	32.10
Hull	26.21	4.21	0.022	34.89
Pongamia pinnata				
Whole seed	15.53	11.76	0.040	47.784
Kernel	6.47	9.004	0.065	40.214
Hull	78.19	0.0010	0.017	45.014

3.3. Slagging and fouling indices

The fouling and slagging predictions in terms of empirical indices (Table 6) were based on the elemental composition analysis of the ashes (Table 5). Deposition tendencies were determined as per the reported literature (Carpenter, 1998). When $B/A < 0.5$ deposition tendency is low, when $0.5 < B/A < 1$ deposition tendency is medium and when $B/A > 1$ deposition tendency is high. For values < 0.31 or > 3 of silica-alumina and iron-calcium ratios deposition tendency is low, while for values between 0.3 and 3 deposition tendency is high. When $S < 0.6$ deposition tendency is low, when $0.6 < S < 2$ deposition tendency is medium and when $S > 2$ deposition tendency is high. Finally, when $TA < 0.3$ fouling tendency is low, when $0.3 < TA < 0.4$ fouling tendency is medium and when $TA > 0.4$ this tendency is high. Thus, the results observed for present samples indicated that ash-related problems should be expected in boilers using these biomasses, due to the high amounts of alkali they contain, which are known to produce molten salt mixtures on accessible surfaces via vaporization, condensation or secondary reactions, as well as the high base-to-acid ratio (Armesto et al., 2002; Hupa, 2005; Steenari and Lindqvist, 1999). Combustion processes with biomass, especially with herbaceous biomasses which have a high content of alkaline elements are prone to experience slagging, fouling and corrosion. (Jenkins et al., 1998; Bryers, 1996; Nielsen et al., 2000; Michelsen et al., 1998). However, this problem can be overcome through specialized deposition monitoring and blowing control system that are commercially available and can assist significantly with the optimization of the blower operations and the control of ash depositions (Yin et al., 2008). Also, biomass material and their ashes tend to be less erosive and abrasive than more conventional solid biofuel because of lower quartz and pyrite levels. Also, co-combustion with fossil fuel seems to be a more concrete option to overcome those difficulties and to economically expand utilization of biomass fuel (Adanez et al., 2003).

4. Conclusion

As the Jatropha and Karanja oil is gaining popularity as source of biodiesel not only worldwide but also in India, its oilseed residual biomasses would be available abundantly. Various analysis performed on these residual biomasses as well as their pellets in the present study, suggested its suitable characteristics for use as solid biofuel. Wherein, the proximate and ultimate analysis indicated its high biofuel reactivity and low ash and lignin content. The pellet preparation does not require any artificial binder and prepared pellets were having high compressive strength. The calorific values obtained for all pellet samples were higher than other biomasses which are routinely being used, while comparable with that of coal. These results promote the use of these residual biomasses as a solid biofuel and as substitute for coal and other conventional fuels in future. The very less sulfur content in all biomass samples and also low nitrogen content except in kernel sample, suggests the minimum threat of environmental pollution after its combustion. Besides, high slagging and fouling characteristics shown by ashes of samples could be controlled by using proper monitoring conditions. Thus, all these properties combined together have shown that Jatropha and Karanja oilseed residual biomass can act as the potential candidates for solid biofuel production.

Acknowledgements

We are grateful to Agharkar Research Institute, Indian Biodiesel Corporation, Baramati, Pune (M.S) India, for providing Jatropha and Karanja oilseeds. We are also thankful to Dr. D.G. Naik, ARI, Pune for providing CHNS analyser facility. Thanks are also due to Duetech Laboratories, Pune for Compressive strength analysis; Chemtech Laboratories, Pune, for the calorific value determination and Department of Geology, University of Pune for the XRF analysis.

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